RAPID EXPANSION OF NEAR AND SUPERCRITICAL SOLUTIONS CONTAINING CELLULOSE TRIACETATE

A. Blasig and <u>Mark C. Thies</u>*
Clemson University
Department of Chemical Engineering
Center for Advanced Engineering Fibers and Films
Clemson, SC 29634-0909
E-mail: mcths@clemson.edu
FAX: (864) 656-0784

Abstract. RESS experiments were performed on cellulose triacetate (CTA) [M_w = 146,000, PDI = 2.07], a semicrystalline polymer that is typically dry-spun into continuous fibers from a solution consisting primarily of methylene chloride. Phase-behavior measurements for solutions of CTA with ethanol and ethyl acetate indicate that both solvents, when used as compressed liquids, can completely dissolve solid CTA (m.p. ~300 °C) at temperatures of ~ 175 °C. However, ethyl acetate was preferred for RESS experiments over ethanol because of the absence of reactions with CTA. The liquid-liquid phase boundary for the ethyl acetate-CTA system was measured and was found to extend from about 180 °C and 15 bar to 230 °C and 80 bar. RESS experiments were subsequently carried out at polymer concentrations of 0.5, 2, and 5 wt %, with pre-expansion temperatures and pressures corresponding to unsaturated (one liquid phase) and supersaturated (two liquid phases) polymer solutions. In general, RESS experiments produced particles and irregularly-shaped structures when expanding 0.5 and 2 wt % solutions, but significant amounts of fibers when RESS processing 5 wt % solutions. Unsaturated pre-expansion conditions resulted in 0.1-0.5 µm particles and fibers, whereas supersaturated conditions produced 0.5-1.5 µm particles and fibers. Thus, we continue to find that concentration and degree of saturation have a significant impact on the product morphology and size of RESS products.

1. INTRODUCTION

In the Rapid Expansion of Supercritical Solutions, or RESS, a mixture of a supercritical solvent and a nonvolatile solute is rapidly expanded across a throttling device, such as an orifice or a capillary [1-4]. Along the expansion path the solvent density dramatically decreases from liquid-like to gas-like densities, causing the solute to precipitate. This rapid decrease in density leads to both uniform conditions and very high supersaturation ratios in the post-expansion environment, resulting in submicron- and micron-sized particles [1,2] and thin films [3]. When polymers are processed by RESS, fibers can also be formed [4-7]. Several research groups have investigated the effect of RESS processing conditions, such as nozzle geometry and pre-expansion temperature and pressure, on the product morphology and

size of polymers. Lele and Shine[1] concluded that if precipitation of a polymer-rich phase occurs late in the nozzle, the time available for structure formation is short, on the order of 10^{-6} s, and particles are formed. On the other hand, if a polymer-rich phase precipitates upstream of the nozzle, the time available for structure formation is long, on the order of seconds, and fibers are formed. Lele and Shine associated the two time scales with the phase behavior of the solution upstream of the nozzle, and concluded that particles are formed from unsaturated solutions and fibers from saturated, two-phase solutions. More recently, Blasig et al. [7] investigated the effect of concentration and degree of saturation on product morphology and size for the RESS of CO_2 and poly(HDFDA), a CO_2-soluble fluoropolymer. A wide range of polymer concentrations was considered, with both homogeneous and two-phase solutions of 0.5, 2.0, and 5.0 wt % polymer being expanded through a nozzle. Blasig et al. found that fibers were produced from 5 wt % solutions whether the solution was saturated or unsaturated, and therefore concluded that, in contrast to the results of Lele and Shine, concentration rather than the "degree of saturation" was the controlling variable for product morphology in RESS. Degree of saturation, or S, on the other hand, was found to affect product size, with smaller structures formed from unsaturated solutions and larger ones from supersaturated solutions.

In this study we investigated the rapid expansion of cellulose triacetate (CTA) solutions. Currently, CTA fibers are dry-spun from mixtures of methylene chloride and methanol, with methylene chloride now being a highly regulated substance. Our work had two goals: One, the investigation of alternative, more benign processing solvents and two, a determination as to whether the effects of concentration and S observed for the poly(HDFDA) + CO_2 system [7] have general applicability for the rapid expansion of polymer-solvent systems.

2. MATERIALS

Cellulose triacetate (CTA), which has a melting point of ~300 °C, was supplied by Aldrich. The wt. average molecular weight (M_w) of the CTA, as obtained by GPC, was 146,000 with a PDI of 2.07. Ethanol (200 proof) was supplied by the Department of Biological Sciences, Clemson University. Ethyl acetate (99.9 %, HPLC grade) was supplied by Fisher Scientific. 3Å molecular sieve (Mallinckrodt, Grade 564CCGT) was supplied by VWR Scientific Products and was used to keep both solvents free of water.

3. EXPERIMENTAL

Because previous work with RESS has demonstrated that the degree of saturation of the phase(s) to be expanded is a key processing variable, liquid-liquid equilibrium (LLE) phase transitions (commonly called cloud points) were measured before RESS experiments in order to locate the phase boundaries. The technique for measuring cloud points is discussed in detail elsewhere [7], so only a brief description of the technique, with the focus on the differences between CO_2 and the more conventional solvents used in this work, is given here.

CTA and solvent (i.e., ethyl acetate or ethanol) are charged into a variable-volume view cell, which contains a piston that separates the working and process fluids. The solvent is also used as the working fluid and is delivered to the view cell via a high pressure generator (High Pressure Equipment (HiP), model 81-5.75-10) to move the piston and compress the mixture of interest on the other side of the piston. Because cloud-point measurements are performed at temperatures as high as 235 ºC, Teflon O-rings and backup rings are used in the cell. A nitrogen-purged convection oven, designed and constructed at Clemson, provides a constant

temperature environment for the view cell and prevents possible conflagrations due to solvent leaks. A borescope (Olympus Ind., model R100-038-000-50) is positioned in front of the sapphire window for monitoring the mixture inside the cell.

For a typical run, a known amount of polymer and solvent are charged into the variable-volume view cell. The temperature and pressure are increased until a homogeneous, transparent solution is then obtained. To determine cloud-point pressures, the pressure is incrementally decreased until a cloudy solution is obtained. In this work, the cloud-point pressure is defined as the pressure at which the piston inside the view cell first becomes invisible due to the cloudiness of the mixture when lowering the pressure. The piston seal (i.e., the Teflon O-ring) was prone to failure because of the elevated temperatures of operation, so we could not wait for isothermal conditions but had to carry out phase-behavior measurements while constantly increasing the temperature at a rate of 0.1 – 0.5 ºC/min. Temperature and pressure measurements were performed with a calibrated RTD and Heise gauge, respectively, and are believed to be accurate 3 °C and 3 bar, respectively. Finally, as a safety measure a rupture disk was placed downstream of the pressure generator to prevent accidental overpressuring of the system.

A schematic of our RESS apparatus is shown in Figure 1. The phase behavior and RESS apparatus share the same view cell, convection oven, and borescope setup. A syringe pump (Isco, model 500D) is connected to both ends of the view cell because the fluid inside the syringe pump is used both as the solvent and the working fluid. The expansion nozzle is made of stainless steel, and its pinhole (50 µm in diameter and 250 µm long) was drilled by EDM (Electrical Discharge Machining). This nozzle was designed by Weber with a tapered inlet and has a nozzle surface that is even with the surface of the end cap. The latter feature was found to be important for reducing the accumulation of CTA on the nozzle tip. A type-K thermocouple, 0.5 mm in diameter, is located inside the pre-expansion tubing (0.3 cm i.d. x 0.635 cm o.d. x 15.24 cm long) about 2 mm upstream of the nozzle. As shown in Figure 1, heating tapes are used to obtain a constant temperature upstream of the nozzle. The third heating tape is wrapped around the pre-expansion tubing and the nozzle, and is controlled by a PID controller (Omega Engineering, model 76000). The sensing thermocouple for the controller (T_4 in Figure 1) is located inside the pre-expansion tubing. With this arrangement, the pre-expansion temperature was controlled to within ±2 ºC. The pre-expansion pressure was controlled by the syringe pump to within ±0.35 bar and measured with a calibrated 0-10,000 psig Heise pressure gauge (labeled P_1) located upstream of the nozzle. A 0.5-µm filter (Alltech Associates, Model 9200) was used to prevent clogging of the nozzle due to impurities. A second pressure gauge (P_2) was used to verify that the pressure had not changed significantly due to possible plugging of the filter.

For a typical RESS experiment, the view cell is charged with a known amount of CTA and solvent. Next, the contents of the cell are compressed with the solvent (now used as the working fluid) from the syringe pump to the desired pressure, and the valve on the process side of the cell is closed. The convection oven is used to heat the view cell to the desired temperature, with magnetic stirring being used to obtain a homogeneous solution inside the cell. Pure solvent is then delivered from the pump and expanded through the nozzle into a 500 ml glass kettle, by-passing the view cell by means of the three-way valve (see Figure 1), all while maintaining a constant pressure on the working-fluid side of the view cell. A heating mantle powered by an on-off controller is used to heat the collection kettle to ~100 ºC to prevent condensation of the solvent in the kettle. This pure-fluid expansion continues until steady state (i.e., a constant pre-expansion temperature and pressure and desired kettle temperature) is achieved, which usually takes about 30 minutes.
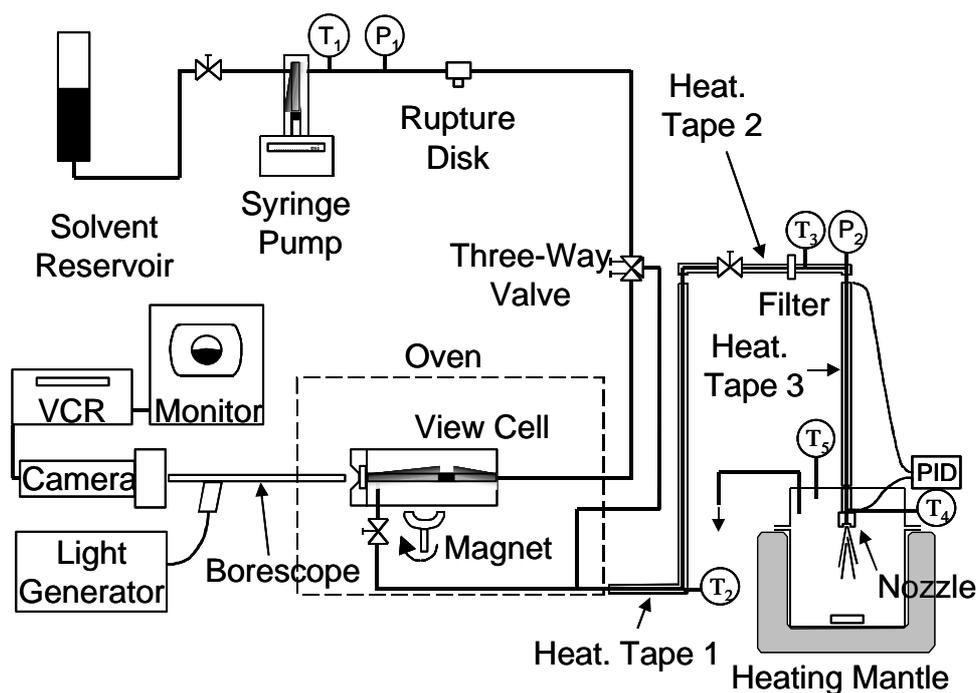
Figure 1. Schematic of the RESS apparatus.

In the meantime, two 500 ml glass kettles, each holding an aluminum SEM specimen stage covered with carbon tape, are pre-heated to ~ 100 °C using additional heating mantles. To initiate actual RESS experiments, the first kettle is exchanged with one of the two pre-heated collection kettles. Then pure solvent flow is diverted exclusively to the working-fluid side of the view cell by means of the three-way valve, and the valve on the process side of the view cell is opened, pushing the polymer-solvent solution out of the cell, through the nozzle and into the glass kettle, which is maintained at ambient pressures. The polymer precipitate is collected onto the aluminum SEM specimen stage, and the gasified solvent is withdrawn from the kettle. Two samples per run are collected about 10 cm downstream of the nozzle for about one minute each. The samples are then platinum-coated (Anatech LTD, model Hummer[®] 6.2), and the size and morphology of the precipitate are determined by scanning electron microscopy (SEM; Hitachi, model SEM S3500N). Following each experiment, the lines of the RESS apparatus are flushed with solvent at the same conditions (i.e., temperatures and pressure) that were used for the actual RESS experiment for at least 30 min to remove any residual polymer.

4. RESULTS AND DISCUSSION

The first solvent that was considered for the RESS of CTA was ethanol. Although we discovered that compressed liquid ethanol completely dissolves CTA at ~160 °C, GC/MS analysis indicates that it reacts with the CTA at these elevated temperatures to form significant amounts (~ 10 wt % of the original ethanol) of ethyl acetate. Thus, no RESS experiments were performed for the CTA-ethanol system.

By carrying out phase behavior measurements in the view cell, we also discovered that compressed liquid ethyl acetate completely dissolves CTA at temperatures of ~175 ºC. The solvent recovered after phase-behavior measurements was analyzed by GC/MS and showed no reaction products for this polymer-solvent system. Cloud-point curves were measured for mixtures of 0.5, 2, and, 5 wt % CTA in ethyl acetate over a temperature range of 185-235 ºC and are shown in Figure 2. The LLE curves show typical LCST behavior with a slope of 1.35 bar/ºC.

Based on the measured cloud-point curves, pre-expansion conditions for RESS were chosen, with unsaturated and supersaturated conditions being equally weighted (see Figure 2). For each of the four RESS conditions selected, polymer concentrations of 0.5, 2, and 5 wt % were investigated to give a total of 12 experimental runs; several of these runs were duplicated to check reproducibility. Originally, a nozzle with a recessed outlet [7] was used for RESS experiments, but the expanding polymer solutions precipitated onto the end cap and eventually grew into the free jet. This behavior was not observed with Weber's nozzle because the nozzle surface was designed to be even with the surface of the end cap. Note that the original nozzle design was used in our previous work [7] with the CO_2-soluble fluoropolymer, but we never observed any precipitation on the end cap.

In general, RESS experiments produced particles and irregularly-shaped structures when expanding 0.5 and 2 wt % solutions, but significant amounts of fibers when RESS processing 5 wt % solutions. Unsaturated pre-expansion conditions resulted in 0.1-0.5 μm particles and
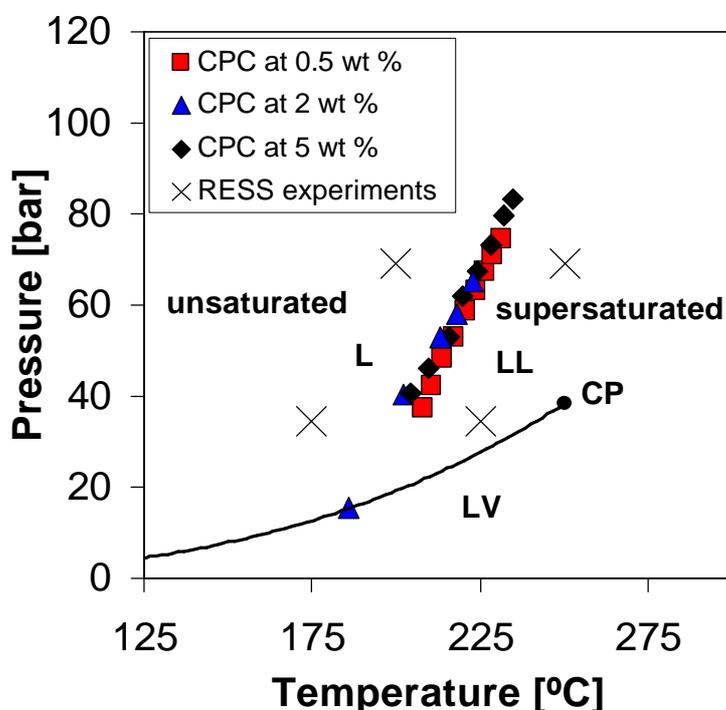
Figure 2. Experimental design for our RESS experiments. Selected experimental pre-expansion conditions (X) are shown in relation to the measured cloud-point curves (CPC) for 0.5, 2, and 5 wt % CTA in ethyl acetate.

fibers, whereas supersaturated conditions produced 0.5-1.5 μm particles and fibers. The irregularly shaped structures are several microns in size and were found only at unsaturated conditions. We believe that reduced solvent diffusion in the free jet at colder unsaturated pre-expansion conditions leads to the formation of soft, solvent-containing particles, which then can fuse together into irregularly shaped structures when particles collide with each other.

5. CONCLUSIONS

Cellulose triacetate has been rapidly expanded with ethyl acetate at near and supercritical conditions, producing both fibers and particles. The effects of concentration and degree of saturation (concentration affects product morphology, degree of saturation affects product size) that were previously observed for the system CO_2 + poly (HDFDA) were found to also apply to this system. Finally, hot ethyl acetate is a viable replacement solvent for methylene chloride for the processing of CTA.

ACKNOWLEDGMENTS

REFERENCES

[1] Lele, A. K., Shine, A. D., Effect of RESS Dynamics on Polymer Morphology. Ind. Eng. Chem. Res., Vol. 33, **1994**, p. 1476.
[2] Türk, M., Formation of Small Organic Particles by RESS: Experimental and Theoretical Investigations. J. Supercrit. Fluid, Vol. 15, **1999**, p. 79.
[3] Matson, D. W., Fulton, J. L., Petersen, R. C., Smith, R. D., Rapid Expansion of Supercritical Fluid Solutions: Solute Formation of Powders, Thin Films, and Fibers. Ind. Eng. Chem. Res., Vol. 26, **1987**, p. 2298.
[4] Han, S. J., Lohse, D. J., Radosz, M., Sperling, L. H., Morphologies of Blends of Isotactic Polypropylene and Ethylene Copolymer by Rapid Expansion of Supercritical Solution and Isobaric Crystallization from Supercritical Solution. J. Appl. Polym. Sci., Vol. 77, **2000**, p. 1478.
[5] Mawson, S., Johnston, K. P., Combes, J. R., DeSimone, J. M., Formation of Poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) Submicron Fibers and Particles from Supercritical Carbon Dioxide Solutions. Macromolecules, Vol. 28, **1995**, p. 3182.
[6] Aniedobe, N. E., Thies, M. C., Formation of Cellulose Acetate Fibers by the Rapid Expansion of Supercritical Methanol Solutions. Macromolecules, Vol. 30, **1997**, p. 2792.
[7] Blasig, A., Thies, M. C., Effect of Concentration and Degree of Saturation on RESS of a CO_2-Soluble Fluoropolymer. Ind. Eng. Chem. Res., Vol. 41, **2002**, p. 4976.